Chapter-1: Introduction

During the last century, the semiconductor and thermo electric materials are the two most eligible candidates of research for physicists and electronic industries. Developing and improving new materials have been made considerably easier by advances in materials science and technology. The more recent technologies are involved in nuclear engineering, computer gadgets and automation engineering, in addition to space flight and missiles research. As a result, new materials are needed that can withstand conditions that were not previously anticipated. It was at this point realized that these two extreme groups, metals and insulators, had been bridged by a new and fundamental approach to materials which enjoy diverse technical applications. One of the most versatile classes of materials known to man is the semiconductor family, including those synthesized in the laboratory. Si and Ge are the most elemental semiconductors.

Compound semiconductors are classified according to their band gap: Semiconductors with a wide and those with narrow band gap. The band gap might be either direct or indirect. Wide band gap compounds are typically those with band gaps more than 0.5 eV and less than 3 eV and those with band gaps greater than 3 eV have insulating or near insulating properties. Compounds such as InSb, PbSe, SnTe, PbTe, and others exhibit narrow band gaps as low as 0.18 eV (InSb). The materials in this study correspond to the group III-V compounds, which have narrow band gaps. A large number of researchers worldwide are working on group III-V semiconductors, especially on semiconductors with a small band gap. Low band gap semiconductors are used in a wide range of applications, including pollution monitoring, gas leak detection, gas sensing and spectroscopy. Covering the near infrared (IR) range is becoming increasingly critical for military, industrial control, medical diagnostics and other civilian needs [1-4]. These semiconductors also work as thermal detectors in the field of Infrared Investigation (IR). In addition, IR systems are highly in demand in the commercial market for use in medical diagnosis, aircraft and automobile safety and quality control of industrial products. An IR detector plays important role as a transducer which converts electromagnetic radiations to measurable electrical signals. IR spectrum offers possibilities beyond human visual capabilities [5].

This field has a great potential in other emerging areas of technology, including missile seeker guidance, target acquisition, search and track etc. As a result of space exploration requirements, lead chalcogenides have been developed for improvements in sensitivity at the medium wavelength infrared (MWIR) atmospheric window starting in the 1950S. Lack of affordable non-renewable fuels has been posing alarming threat to energy security, environmental pollution and global warming. Thermoelectric energy conversion effect directly converts heat energy or electric energy into electric energy or heat energy, respectively. Hence, active research and innovations continue to foster the exploration of solar energy, geothermal power, bio fuel, etc. All of them can be exploited to some extent but perhaps the most plentiful is solar energy to be converted, which involves semiconductor materials for conversion of electromagnetic energy into electric current using photovoltaic [6].

Binary compounds formed from group IV and VI elements, such as PbS, PbTe and SnS are narrow gap semiconductors. On doping with group V or VI elements, they transform into semiconductors with narrower band gap becoming suitable candidates for infrared devices. Infrared spectroscopy is a complex and adaptable technology and one of its most important properties is its qualitative aspects. The acquired results demonstrate that all of the IR spectra are nearly identical and agree with the available literature data [7]. On the other hand, the V-VI compounds like Bi_2Te_3, Sb_2Te_3 and Bi_2Se_3 which do possess narrow band gaps also exhibit thermoelectric properties [8-11].

In recent years, there has been observed a renewed interest in long wavelength infrared bands. Furthermore, modified semi-conductor alloys belonging to groups III-V, IV-VI and II-VI, such as indium antimonide and mercury cadmium telluride (MCT), find use as LWIR spectral response materials. InSb materials with narrow band gap were developed consequent to microstructure changes and weak Hg-Te bonds by thermal, compositional and lattice instabilities in MCT systems [12-13]. By adopting an appropriate crystal growth process and doping with appropriate elements, InBi can be customized to modify its structural, electrical, optical and mechanical properties [14].

1.1 Overview on Materials:

As per electronic band theory, materials can be classified as insulators, semiconductors, semi-metals or metals. A semi-metal has a negligible density of states at the Fermi level. It has no band gap due to the overlap, though very small, between the conduction and valence bands. In a semi-metal, the bottom of the conduction band is typically situated in a different part of momentum space (at a different **k**-vectors) from the top of the valence band. One could say that a semi-metal is a semiconductor with a negative indirect band gap.

Indium (In)

Indium is a silvery white, a soft, ductile, malleable and lustrous metal. Its low melting point offers its major use in indium alloys. It is typically found in zinc, iron, lead and copper ores. According to the U.S. Geological Survey (USGS), it is three times more abundant than silver or mercury. Indium has been reported to have better permeability and conductivity as a result it finds tremendous application in the glassy compound (ITO). High-purity oxides of indium and tin are used to make transparent and conductive electrodes applicative in the plasma TV and LCD TV screen industries. It also finds application as a sensitive element for some gas measurements. Indium has the characteristics of high boiling point, low resistance, and corrosion resistance. Because of this, it is widely used in the electronic semiconductor industry to produce semiconductor materials. Majority of the global indium is consumed to produce ITO targets.

Due to its low melting point, Indium can be used to produce a variety of fusible alloys. Such indium-containing alloys with a melting point in the range of 47 to 122 °C are mostly used to manufacture various fuses, temperature controllers, and signaling devices. Indium alloys can be used for production of solar cells too. Copper indium gallium selenium thin-film solar cells have the characteristics of low production cost, low pollution, and good performance under low light. The photoelectric conversion efficiency ranks first among various thin-film solar cells, and is internationally known as a very promising new thin-film solar cell. Many fusible alloys of indium are used as brazing materials. With indium, parts made of piezoelectric materials can be firmly welded to one another. In the manufacture of multilayer integrated circuits, the selection of brazing materials containing indium is a crucial step.

Bismuth (Bi)

Bismuth is hard, brittle, lustrous, and coarsely crystalline. P-type doping of elemental bismuth with indium, gallium and tin: a novel doping mechanism in solids. For a very long time, several theoretical and experimental research have focused on the electrical characteristics of Bi, just like they have with the group-V semi-metals As and Sb. Bismuth is a prototype semi-metal: its structure is non cubic and rather complicated; however, the packing density is comparable to that in metals. The band structure of Bi was investigated experimentally [15-21]. The study shows Bi a semi-metal with a small band overlap (~ 37 meV at 4.2 K) and a small and equal number of electrons and holes 3 x 10^{17}cm $^{-3}$ at 4.2 K, 3 x 10^{18} cm^{-3} at 300 K[22].

Due to their peculiar thermoelectric and thermo magnetic effects at cryogenic temperatures as well as their semi-conducting qualities, bismuth and antimony alloys have received a lot of interest [23].

Alloys based on bismuth-telluride are frequently used to create high performance thermoelectric generators. They have been employed in thermoelectric refrigerators for the temperature control of semiconductor devices such as laser diodes or CCDs (charge coupled devices) due to their outstanding performance at room temperature as compared to other thermoelectric materials [24].

Tellurium (Te)

Tellurium is a semi metallic, lustrous, crystalline, brittle, silver-white element. Tellurium is not found it abundance with approximately 0.001 parts per million in earth's crust. Tellurium minerals include calaverite, sylvanite and tellurite. It is obtained commercially from the anode muds produced during the electrolytic refining of copper. These contain up to about 8% tellurium.

Tellurium has been used to vulcanize rubber, to tint glass and ceramics, in solar cells, in rewritable CDs and DVDs and as a catalyst in oil refining. It can be doped with silver, gold, copper or tin in semiconductor applications. Tellurium is added to lead to improve its durability, strength and resistance to corrosion. It can be used for cast iron, ceramics, blasting caps, solar panels, chalcogenides glasses. In table 1.1 mentioned the properties of In, Bi and Te element

Table 1.1 Properties of In, Bi and Te element

Sr. No.	Physical Properties	In	Bi	Te
1	Crystal structure	Face-centered tetragonal	Rombohedral	Simple Trigonal
2	Space group	I4/mmm	$R\bar{\bar{3}}m$	P 3121
3	Melting point	156.6 °C	271.3 °C	449.51 °C
4	Material type	post-transition metal	post-transition metal	Semiconductor

The possibility to modify physical properties of III-V compounds provides ample opportunity for research and development of devices with improved efficiency. InBi is an exception amid the III-V category due to its low melting point, lack of polymorphism and semi-metallic conductivity [25, 26]. Anosov et al first time reported the existence of the berthollide type intermetallic compound InBi in 1947[27]. Phase diagram of InBi (fig. 2) indicates that it occurs at 50% of each element in the In-Bi system describes melting point 109.5 °C [28] and its density is 8.84 gm / cm^{-3}. The InBi crystal has a tetragonal unit cell figure 1 [29]. It forms the Ditetragonal-bipyramidal point symmetry group (i.e. 4/mmm). They also obtained its space group as P4/nmm with a = b = 5.000 Å and c = 4.773 Å, thus c/a = 0.9546 [30-33]. At room temperature, the intermetallic compound InBi displays divalent behaviour and its magnetic susceptibility is approximately ~ 50 emu/mole. Its resistivity is of the order of 10^{-4} ohm/m.

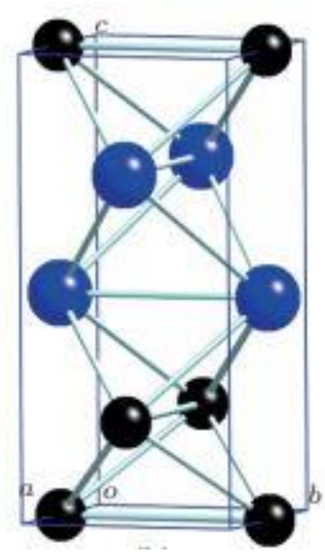

Figure 1.1: InBi crystal structure: tetragonal P4/nmm phases. The large blue and small black spheres represent Bi and In atoms, respectively.[30]

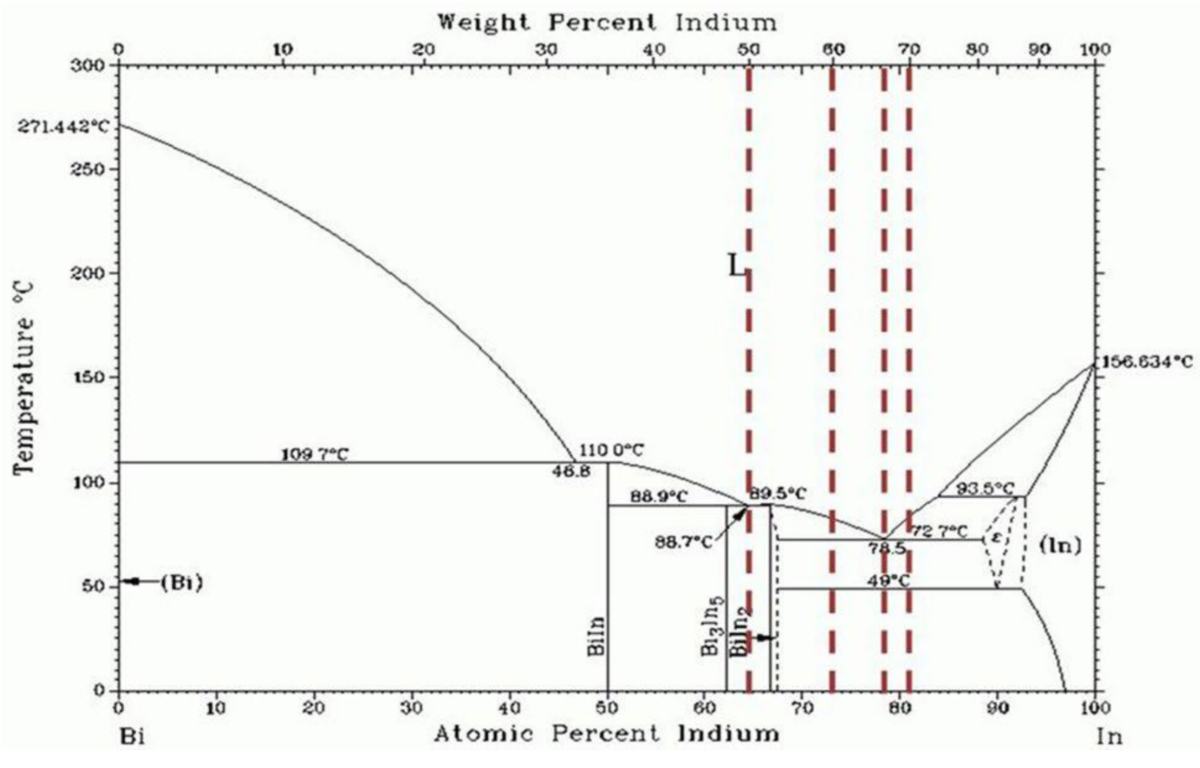

Figure 1.2: Phase diagram of InBi [39]

On doping with group V or VI elements, InBi transforms into a narrow band gap semiconductor making it a reliable candidate for infrared devices. InBi is semi-metallic in nature with optical band gap of -1.5 eV at room temperature as reported by Berding.[14]

Different authors have employed the Bridgman and zone melting procedures to generate an InBi single crystal. Structural, electrical, optical and mechanical properties of InBi can be fine-tuned by adopting appropriate crystal growth processes as well as doping with suitable elements [34-39].

1.2 Overview on Crystal growth

Crystals are useful mainly because they have regular internal structures, and they often exhibit anisotropic properties, i.e. the properties of a crystal vary depending on the direction along which measurements are made. It is possible to have non-crystalline semiconductors. A huge, extremely pure single crystal of silicon is one of the most essential uses of single crystals in science and technology - these get sliced up as soon as they grow and are used in microelectronics as well as computer chips. Some optical devices are made from crystals, such as polarizers or frequency doublers. It is very important in biological sciences to grow crystals of proteins because of their structure, as well as the applications they can be used for. This gives us an understanding of how proteins are built and how they function. This is extremely interesting information. Since proteins perform just about all functions in our bodies on a molecular level.

Crystals are an unsung pillar of modern technology. Today's technological advances are largely dependent on the availability of appropriate single crystals, whether they are for lasers, semiconductors, magnetic devices, optical devices [40]. Several well-written books are accessible on subjects such as the foundations of crystal growth [41], the various techniques of crystal growth, their hypotheses, analyses, and use [42-46], and their interpretation of the mechanism of growth and related topics [47-56]. A rapid development of structural crystallography, crystal chemistry, and crystal physics was due to the analysis of crystal structures of most solid materials. It was essential to have a detailed understanding of the atomic arrangements, chemical bonds, and the symmetry-property and structure-property relationships. The study of crystals has also developed with increasing interest in understanding the origins of various types of crystals, that is, to understand why and how different crystal morphologies exist.

1.3 Applications of Crystals

- Semiconductor optoelectronics (substrate materials): Transistors, diodes, integrated circuits: Si, Ge, GaAs, InP LEDs and lasers: GaAs, GaInAs, GaInP, GaAsP, GaP:N, ruby; Solar cells: Si, GaAs, GaInP / GaAs.
- Non-glass optics: alkali halides, alkaline earth halides, thallium halides, Ge, sapphire

- Electromechanical transducers Ultrasonic generators, sonar: ADP, KDP Strain gauges: Si Optical modulators: $LiNbO_3$, $BaTiO_3$, $BaNaNiO_3$Piezoelectric microphone sources: quartz
- Radiation detectors: HgI_2, NaI:Tl, CsI:Tl, LiI:Eu, Si, Ge.
- Artificial gems: sapphire, ruby, TiO_2, ZrO_2

1.4 OBJECTIVES

The present study aims to modify the properties of InBi with Te doping. Following is the aim of the present study:

- To study the growth and characterization of pure and three different Te doped InBi crystals.
- To confirm distribution of elements in the doped crystals.
- To determine optical band gap
- To determine Seeback co-efficient.
- To determine Hall coefficient and carrier concentration.
- To determine Vickers micro hardness under various parameters.

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